

U.S. DEPARTMENT OF COMMERCE  
National Technical Information Service

PB-299 373

# **Application of Advanced Technology for NO<sub>x</sub> Control: Alternate Fuels and Fluidized-Bed Coal Combustion**

**Massachusetts Inst of Tech, Cambridge**

**Prepared for**

**Industrial Environmental Research Lab, Research Triangle Park, NC**

**1978**

| TECHNICAL REPORT DATA<br>(Please read instructions on the reverse before completing)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                          |                                                                 |
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| 1. REPORT NO.<br>EPA-600/J-77-155                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 2. JOURNAL ARTICLE                                                                                                       | 3. PB 299373                                                    |
| 4. TITLE AND SUBTITLE<br>Application of Advanced Technology for NOx Control:<br>Alternate Fuels and Fluidized-Bed Coal Combustion.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                          | 5. REPORT DATE                                                  |
| 7. AUTHOR(S)<br>J.M. Beer(MIT), and G.B. Martin(IERL-RTP)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                          | 6. PERFORMING ORGANIZATION CODE                                 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Massachusetts Institute of Technology<br>77 Massachusetts Avenue<br>Cambridge, Mass.<br>02139                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                          | 8. PERFORMING ORGANIZATION REPORT NO.                           |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>EPA, Office of Research and Development<br>Industrial Environmental Research Laboratory<br>Research Triangle Park, NC 27711                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                          | 10. PROGRAM ELEMENT NO.                                         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                          | 11. CONTRACT/GRANT NO.                                          |
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|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                          | 14. SPONSORING AGENCY CODE<br>EPA/600/13                        |
| 15. SUPPLEMENTARY NOTES<br>Presented at the 69th Annual AIChE meeting, Chicago, Ill. (11/30/76)<br>Published in the AIChE Symposium Series, Vol. 75, 1977                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                          |                                                                 |
| 16. ABSTRACT<br>The paper discusses the effect of alternate fuels and Fluidized coal combustion in controlling the emission of nitrogen oxides (NOx). The current trend in energy use in the U.S. is toward greater use of coal and coal derived fuels, and on ensuring that these fuels are produced and burned in an environmentally acceptable manner. Three approaches are being pursued to control pollutant emissions: direct coal combustion in conventional boilers with stack gas desulfurization; fluid-bed coal combustion with desulfurization in the bed; and conversion or cleaning to remove sulfur from the fuel before combustion. The major pollutants to be controlled are particulate, sulfur oxides (SOx) and NOx. Each approach is distinguished by its method of SOx control. The particulate control method also depends on the specific approach. However, the techniques for NOx control have a common basis for all three approaches; that is, altering the conditions under which combustion takes place.<br>Combustion process modification is the most widely accepted method for control of NOx from stationary sources. Much knowledge has been accumulated on both experimental and practical systems directly fired with coal and other fossil fuels; however, attention has only recently turned to alternate methods for coal utilization. For that reason, this paper emphasizes describing available information both on emission characteristics of clean(low sulfur) coal derived gaseous and liquid fuels and on direct coal combustion in fluidized beds. |                                                                                                                          |                                                                 |
| 17. KEY WORDS AND DOCUMENT ANALYSIS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                          |                                                                 |
| a. DESCRIPTORS<br>Pollution<br>Nitrogen Oxides<br>Combustion<br>Fluidized Bed Processing<br>Gasification<br>Liquefaction                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | b. IDENTIFIERS/OPEN ENDED TERMS<br>Pollution Control<br>Stationary Sources<br>Alternate Fuels<br>Combustion Modification | c. COSATI Field/Group<br>13B<br>07B<br>21B<br>13G<br>07A<br>07D |
| 18. DISTRIBUTION STATEMENT<br>Release to Public                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 19. SECURITY CLASS (This Report)<br>Unclassified                                                                         | 21. NO. OF PAGES<br>23                                          |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 20. SECURITY CLASS (This page)<br>Unclassified                                                                           | 22. PRICE<br>A02-A01                                            |

# APPLICATION OF ADVANCED TECHNOLOGY FOR NO<sub>x</sub> CONTROL: ALTERNATE FUELS AND FLUIDIZED-BED COAL COMBUSTION

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## INTRODUCTION

The current trend in energy use in the U.S. is toward greater utilization of coal and coal-derived fuels. There is also a strong emphasis on ensuring that these fuels are produced and burned in an environmentally acceptable manner. Three approaches are being pursued for control of pollutant emissions:

- (1) direct combustion of coal in conventional boilers with stack gas desulfurization,
- (2) fluidized bed combustion with desulfurization in the bed, and
- (3) conversion or cleaning of the coal to remove sulfur from the fuel prior to combustion.

The major pollutants to be controlled are in the form of particulate, sulfur oxides (SO<sub>x</sub>), and nitrogen oxides (NO<sub>x</sub>). As can be seen above, each approach is distinguished by its method of control of SO<sub>x</sub>. The method of particulate control is also dependent on the specific approach. However, the techniques for control of NO<sub>x</sub> have a common basis for all three approaches, that is, alteration of the conditions under which combustion takes place.

Based on many past and present studies, modification of the combustion process is the most widely accredited method for control of NO<sub>x</sub> from stationary combustion sources. A large body of knowledge has been accumulated on both experimental and practical systems directly fired with coal and other fossil fuels;

however, attention has only recently turned to alternate methods for coal utilization. For that reason, the emphasis in this paper is on describing the information available both on emission characteristics of clean (low sulfur) coal-derived gaseous and liquid fuels and on direct coal combustion in fluidized beds. It discusses the potential applications of existing control techniques to alternate fuels and their extension to fluidized beds.

## BACKGROUND

The mechanisms of formation and techniques for control of NO<sub>x</sub> have been extensively discussed (1, 2, 3, 4, 5); however, a brief summary is in order. (Note that subsequent discussion will be limited to nitric oxide (NO), which is the primary form of NO<sub>x</sub> found in the flue gas of most conventional combustion equipment.)

### Mechanisms

The mechanisms for formation and destruction of NO are as follows:

- (1) Thermal NO is formed from fixation of atmospheric nitrogen by Zeldovitch reactions, which have a strong temperature dependence.
- (2) Nitrogen species (e.g., HCN, NH<sub>3</sub>) can be synthesized from N<sub>2</sub> (6, 7) in fuel-rich regions of the flame and subsequently oxidized to NO.
- (3) Fuel NO is formed by oxidation of chemically

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TABLE 3. COMPARISON OF VARIOUS LIQUID FUELS (8)

| Fuel              | Higher heating value | Ultimate analysis, Wt. % |      |       |       |      |
|-------------------|----------------------|--------------------------|------|-------|-------|------|
|                   | KJ/Kg                | C                        | H    | N     | S     | O    |
| Distillate oil    | 44,892               | 86.9                     | 13.1 | 0.023 | 0.096 | 0.0  |
| Residual oil      | 44,147               | 86.8                     | 12.5 | 0.22  | 0.89  | 0.0  |
| COED crude        | —                    | 83.0                     | 8.4  | 1.1   | 0.35  | 7.15 |
| COED hydrotreated | —                    | 88.0                     | 11.6 | 0.01  | 0.01  | 0.38 |
| Synthoil          | 39,077               | 89.6                     | 7.6  | 0.9   | 0.31  | 1.6  |
| H-coal crude      | —                    | —                        | 9.5  | 0.68  | 0.19  | —    |
| H-coal low sulfur | —                    | —                        | 8.4  | 1.05  | 0.43  | —    |
| Toscoal oil       | 37,681               | 80.7                     | 9.1  | 0.7   | 0.2   | 9.4  |
| Shale oil         | 43,496               | 84.6                     | 11.7 | 1.77  | 0.76  | —    |
| Alcohol fuel      | 22,278               | 37.5                     | 12.5 | 0.0   | 0.0   | 50.0 |

be considered as supplements or replacements for natural gas and light fuel oils and may be used predominantly in combustion equipment currently burning these fuels (e.g., residential, commercial, and small industrial boilers). SNG is produced to be similar to natural gas. The alcohol fuels will be predominantly methanol, possibly with up to 10% higher alcohol. The heavy synthetic oils may be used as boiler fuels or may be distilled to produce light fuels suitable for turbines or residential furnaces.

#### Medium-B.t.u. Gas

This is the product of oxygen-blown gasifier systems and is currently projected primarily as a synthesis gas for production of SNG and methanol. Its use as a boiler fuel may depend more on economics than on technical considerations.

#### Low-B.t.u. Gas

Although these fuels are identified by the single term low-B.t.u. gas (LBG), the actual nature of the fuels is as varied as the air-blown gasification systems that can be used to produce it. It is projected primarily as a fuel utilized in utility boilers or by industrial parks, either of which could be located close to the gasification site, since long distance transportation is not economical. The actual utilization projected for the LBG depends on the time frame. In the near term it may be used in conventional utility boilers and gas turbines either as retrofit to existing systems or in integrated new designs. However, in the long run, combined cycles based on supercharged boilers or high temperature gas turbines as the primary combustion device may predominate. To increase the efficiency of advanced design gasifier systems, there is a strong interest in high-temperature gas turbines as the primary combustion device. To increase the efficiency of advanced design gasifier systems, there is also a strong interest in high-

temperature  $H_2S$  removal processes to provide a clean fuel gas at 537° to 817°C. Again, both economics (capital cost and energy efficiency) and technology may come into play in the final decision.

#### Trace Constituents

The fate of the sulfur is fairly well considered in most studies of medium- and low-B.t.u. gases, and removal of  $H_2S$  and COS is well documented. On the other hand, the fate of the nitrogen content of the coal has received less attention. Farnsworth (9) shows the final concentration of bound nitrogen species in the medium-B.t.u. gas after low-temperature cleanup from the Koppers-Totzek process to be less than 1 p.p.m. On the other hand, there is considerable evidence of the presence of large amounts of  $NH_3$  in the product gases (10). Robson (11) estimates up to 600 p.p.m. of  $NH_3$  in a low-B.t.u. gas with a low-temperature  $H_2S$  cleanup and up to 3,800 p.p.m. from high-temperature processes under development. It is not clear that these nitrogen compounds could be present in the high-B.t.u. fuels; however, it is quite possible that they be present in the low- and medium-B.t.u. gaseous fuels. Finally, many coal conversion systems producing gaseous fuels also form significant amounts of heavy organic tars, and there is indication that some of this material may be present in the fuel gas after cleanup. This tar may also contain bound nitrogen compounds (12).

## DISCUSSION

The discussion is divided into two sections, dealing with alternate fuel combustion and fluidized-bed combustion.

#### Combustion and Emission Characteristics of Alternate Fuels

Each of the candidate fuels has its own distinct combustion characteristics, pollutant emission potential,

and operating constraints. Since these fuels have only recently been considered for widespread application to stationary combustion sources, there is scarcity of experimental combustion and emission information and these characteristics have not been documented for any practical system operating on these fuels. The most recent available data are summarized below and related information for each fuel is discussed.

### Synthetic Natural Gas

The composition of synthetic natural gas (SNG) is normally shown as closely approximating that of natural gas (i.e., principally methane) with all trace contaminants (e.g., H<sub>2</sub>S, NH<sub>3</sub>) removed. If this is the case, combustion and emission properties are well known and thermal NO control technology for utility boilers is well established.

### Alcohol Fuels

The alcohol fuels under consideration are predominantly methanol or mixtures of methanol and higher alcohols. Limited results on combustion of methyl fuel in an unspecified system as reported by Duhl (12) show NO levels to be about a factor of 4 less than those for methane. Duhl has subsequently reported on methanol combustion in a 50-MW utility boiler and shows only minor differences in emissions of methanol (about 60 p.p.m. NO) and natural gas (about 75 p.p.m.) at comparable conditions (14). Martin has presented a summary of in-house and contract research on methanol combustion (15) and the results can be summarized as follows:

- (1) For any given condition alcohol fuels produce lower emissions of NO<sub>x</sub> than distillate oil, methane, or propane.

- (2) The NO emissions of alcohol fuels increase as the percentage of higher alcohols increases.

- (3) The low NO emissions for alcohol fuels appear to be a function of the presence and level of oxygen in the fuel molecule, which can be viewed as a diluent carried in the fuel. The operative mechanism appears to be related to thermal effects of the fuel, latent heat of vaporization, and/or decreased flame temperature; however, chemical effects cannot be totally ruled out.

- (4) The magnitude of the difference between methanol and any conventional fuel is a characteristic of system design; however, the difference appears to be smaller for cold-wall systems.

- (5) The emissions of CO, UHC, and particulate from alcohol fuels were generally the same as, or less than, those for the conventional clean fuels tested (propane and distillate oil). Aldehydes do not appear to be a significant problem based on limited data.

- (6) From a technical standpoint, methanol

appears to be a satisfactory fuel for stationary combustion systems; however, the final commercial feasibility will probably depend more on cost and availability than on the ability to burn the fuel.

### Synthetic Oil Products

The data on combustion of synthetic oils derived from coal and shale containing high levels of chemically bound nitrogen (> 1%) are very limited. Some data have been reported on lower nitrogen (< 0.5%) coal oils by Haebig (16) and on a range of shale oils (0.18 to 2.05% N) by Dzuna (17) for a small atmospheric pressure burner. Hardin has reported coal oil data for a gas turbine combustor (18).

Haebig used a small firebrick chamber, fired by a modified flame retention residential oil burner with an air-atomizing nozzle. The heat input rate was a nominal 1 ml per sec. of oil. Emissions from three coal-derived fuels were measured and compared to those from conventional distillate oil. The coal-derived oils consisted of one distilled product with 0.31% nitrogen and two full-range filtered crudes with about 0.5% nitrogen. The fuel nitrogen conversion trends are similar to those previously reported for doped distillate by Martin (19) and for petroleum-derived residual oils by Turner (20). One particularly significant point is that the distillate from the full-range coal liquids contained 0.31% nitrogen, apparently indicating that the nitrogen compounds are considerably lower boiling fractions compared to those found in conventional crudes (i.e., Haebig found only 0.01% N in a conventional distillate). At low excess-air levels significantly higher fractional conversion of the nitrogen to NO was observed for the 0.3% distillate than for the 0.5% N full-range crude. It was also observed that, when the petroleum-based distillate oil was doped to 0.5% N with pyridine, the fractional conversion was more similar to the coal distillate than to the full-range oil. Both of these observations may indicate a higher conversion of more volatile nitrogen compounds and the greater possibility of controlling the formation of fuel NO from synthetic oils through combustion control, as discussed by Martin previously (8).

Dzuna used the same system to test both full-range and distillate-fraction shale oils which had been subjected to a range of hydrotreatment from mild to severe. The full-range nitrogen content ranged from 2.5 to 0.27% N, while that in the distillate fraction ranged from 1.60 to 0.18%, dependent on the extent of treatment. It was concluded that these fuels exhibited combustion and NO<sub>x</sub> emission characteristics very similar to those of petroleum-derived oils. The NO<sub>x</sub> emissions were a function of fuel nitrogen content, and a maximum level of 1400 p.p.m. NO<sub>x</sub> (corrected to 3% O<sub>2</sub>) was observed for the 2.5% N full-range crude. Another interesting and potentially very significant observation

was that even the full-range crudes exhibited smoke characteristics similar to those of a conventional distillate oil and considerably lower than those of a No. 4 oil tested in the same apparatus. This appears somewhat contrary to speculation that these fuels might present a smoke problem.

Hardin reported the results of combustion of two COED oils (a light fraction and a blend of 20% light and 80% heavy fraction), of "Sea Coal," and of JP4 and 5 fuels in a T63 gas turbine combustor can. The fuel nitrogen contents for the synthetic oils ranged from 0.15% for the 20/80 blend to 0.4% for the "Sea Coal," and total  $\text{NO}_x$  emissions were reported to increase with increased fuel nitrogen. It was also concluded that combustor modification for fuel NO control did not appear promising; however, no specific attempts at modification were discussed. The conclusion was even less surprising if the combustor operated at the very lean conditions stated (i.e., F/A of 0.0117 to 0.022) and with a lean primary combustion zone. The fuel analysis shows 0.19% in the light product and 0.13% in the heavy product, indicating that for the distilled COED oil the nitrogen also concentrates in the lighter fractions.

#### Low-B.t.u. Gas

The combustion data on these fuels are also quite limited; however, some additional data have also become available for both boiler and gas turbine type combustors.

The data from the EPA contract with the International Flame Research Foundation have been presented previously (8); however, to place some subsequent data in context it is appropriate to show these data again. Figure 1 indicates that the simulated low-B.t.u. gas at 25°C, when combusted with 105% of theoretical air at 300°C, resulted in an  $\text{NO}_x$  emission of less than 4 p.p.m. Lisauskas (12) used a small refractory furnace to burn the product gas from a pilot-scale fixed-bed gasifier. The burner was a scaled-down version of a bluff body-stabilized, register-type boiler burner. The fuel gas contained 400 to 1,900 p.p.m.  $\text{NH}_3$ , dependent upon the gasifier operating conditions, and was delivered to the burner at temperatures between 32° and 43°C. The organic tar was removed in most cases. In one case the  $\text{NH}_3$  was scrubbed to the range of 11 to 43 p.p.m. in the fuel gas before combustion to establish the thermal NO baseline. A surprising result is that the baseline level with low-temperature fuel and no air preheat is stated to be 90 to 140 p.p.m. of thermal NO, which is a marked contrast to the IFRF experience. Based on this thermal NO value and the subtraction technique for determination of the fuel NO, the conversion to NO decreases from 65% at 240 p.p.m.  $\text{NH}_3$  in the fuel gas to 23% at 1,900 p.p.m.  $\text{NH}_3$ . Again the trends are generally similar to those

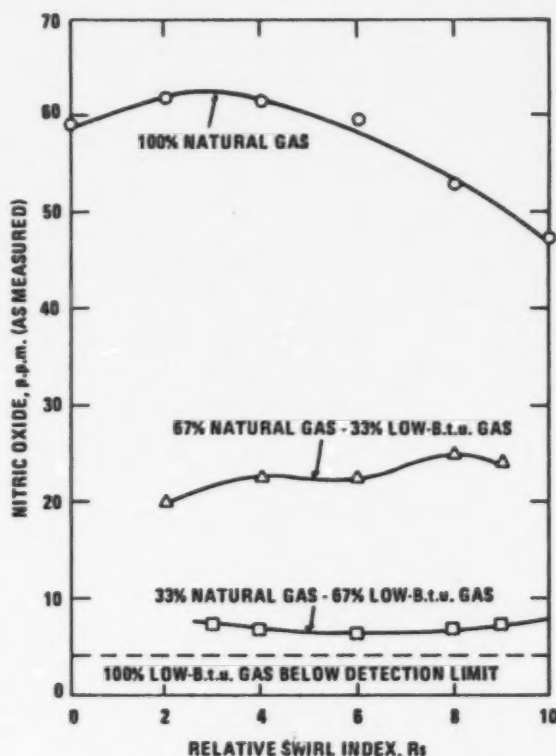


FIG. 1. NITROGEN OXIDE EMISSIONS AS FUNCTIONS OF COMBUSTION AIR SWIRL AND FUEL GAS COMPOSITION.

observed for oils (8, 20). Although some points in the report by Lisauskas are not clear, this is a particularly valuable contribution of data on combustion of a real coal-derived low-B.t.u. gas containing  $\text{NH}_3$ .

Pillsbury (21) has presented results from firing simulated low-B.t.u. gases with heating values from 4,625 to 10,000 KJ/m<sup>3</sup> in subscale and full-sized gas turbine can combustors of similar design. The gases were low-temperature, bound-nitrogen-free blends of pure gases. The results show 5 to 25 p.p.m. NO over the combustor exit temperature range of 647° to 887°C as compared to 30 to 60 p.p.m. for natural gas over the same range of exit temperatures. The CO was found to be greater than for natural gas in the subscale but considerably reduced in the full-sized combustor. These results are similar to those previously reported by Klapatch (22), although it is unclear in both cases on what basis the  $\text{NO}_x$  measurements are reported (i.e., p.p.m. as measured, corrected to some  $\text{O}_2$  level, or some other form).

#### Analysis of Systems Implications

The foregoing summary of available combustion data on alternate fuels shows both that the amount of information on actual alternate fuels is quite limited

and that the studies to date have not considered system design aspects related to pollutant emission control. Emphasis needs to be placed on development and application of known emission control techniques to systems to utilize the alternate fuels. A recent paper by Martin (23) has discussed in detail the use of existing knowledge of control approaches and computational techniques to provide design concepts for low emission combustion systems. While the discussion covers only a limited number of system concepts, it emphasizes the point that efficient, environmentally acceptable use of alternate fuels may necessitate abandoning or substantially modifying current conceptions of combustion systems. When the various fuel conversion schemes with the attendant cost and energy efficiency aspects are compared to conventional fuels the differences are substantial. In view of this, the combustor designer should be prepared to consider alternate concepts that offer substantial emission and/or efficiency benefits, even if the approach departs considerably from conventional practice. The major aspects of the paper are summarized below and additional discussion of key points is provided.

**Liquid Fuels.** The emission control techniques capable of controlling fuel nitrogen conversion of conventional fuels (e.g., staged combustion and burner design) should be applicable to combustion of high-nitrogen synthetic fuels in both boilers and gas turbines; however, more effective applications may have to be developed to handle the higher nitrogen levels. The key feature for liquid fuels may be the way in which the fuel nitrogen compounds are bound in the fuel. For conventional petroleum-derived heavy fuels, the degree of NO<sub>x</sub> control with staged combustion has generally been limited to about 50% by the onset of unacceptable smoke formation in the experiments performed to date. Some encouraging results have recently been generated under EPA Contract 68-02-1500 with Ultrasystems, Inc., where reductions of 65% have been achieved with a high-nitrogen (0.71%) residual oil. The experience with the heavy fuels has generally been less successful than experiments with doped distillate oils, where the nitrogen is 100% volatile, which have resulted in an 80% to 90% fuel NO<sub>x</sub> reduction for a 1% N fuel by staged combustion (see Figure 2).

The limited data available on crude and distillate fractions of several synthetic oils derived from coal suggest that the nitrogen compounds may be more evenly distributed over the boiling range of the oil (16, 17, 18). This can be seen by reference to Table 4. In the case of a high-nitrogen California petroleum crude, the distillate fraction had only about one-tenth the nitrogen concentration of the parent crude (24). For the three synthetic crudes listed the distillate fuels have 0.6 to 1.45 times the nitrogen content of the parent crude. Necessary information that is not given for any of the

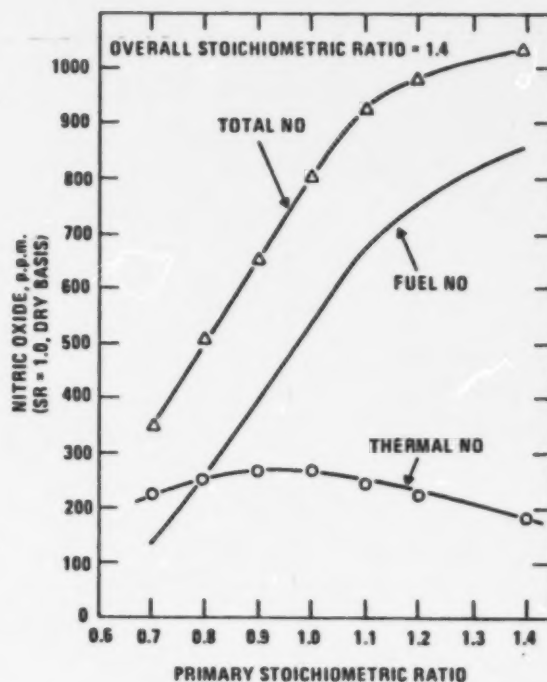


FIG. 2. REDUCTION OF FUEL NO BY STAGED COMBUSTION.

TABLE 4. COMPARISON OF FUEL NITROGEN CONTENT OF CRUDE AND DISTILLATE FRACTIONS OF SYNTHETIC AND PETROLEUM CRUDES

| Fuel                            | Nitrogen content, % |            |
|---------------------------------|---------------------|------------|
|                                 | Crude               | Distillate |
| Wilmington, California oil (24) | 0.65                | 0.07       |
| Coal-derived (16)               | 0.5                 | 0.31       |
| COED coal-derived (18)          | 0.13                | 0.19       |
| Shale-derived (17)              | 2.05                | 1.80       |

fuels is the fraction of the crude that will appear as a light distillate oil. This would allow a better assessment of the volatility of the nitrogen compounds in the crude. In any case the comparison indicates that the synthetic oils have significantly more of the nitrogen distributed into the lighter ends and, therefore, may be more amenable to NO<sub>x</sub> control by staged combustion.

While removal of nitrogen from the synthetic oils by hydrotreating is possible, indications are that hydrotreating would add significantly to the fuel cost. However, there is another aspect of the effect of hydrotreating on fuel properties that must be mentioned, that is, the effect on carbon-to-hydrogen ratio.

Many of the synthetic oils appear to have a carbon-to-hydrogen ratio greater than that found even in residual oils derived from petroleum. This property is believed to be related to smoke production. If significant smoke problems are encountered with crude synthetic oils under staged combustion conditions, it may be desirable to use a mild hydrotreatment to decrease carbon-to-hydrogen ratio as well as to achieve a small reduction in fuel nitrogen. The resultant fuel may be more suited for  $\text{NO}_x$  control by combustion techniques without excessive carbon particulate levels. This hypothesis needs experimental verification.

**Low-B.t.u. Gas.** Although some industrial applications have been discussed, it now appears that low-B.t.u. gases will be used predominantly as a low-sulfur fuel supply for utility power generation. The processes used to convert the fuel gas to electric energy will be either conventional steam power plants or combined cycle systems. These combined cycle systems can be either a supercharged boiler with a recovery gas turbine or a fired gas turbine with waste heat recovery boilers. The latter system appears to be favored for an advanced gas turbine capable of accepting higher turbine inlet temperature (i.e., 1540 to 1640°C). The overall system efficiency (i.e., energy of coal input to energy equivalent of electricity output) is a function of the product of the thermal efficiency of the gasification system and the thermal-to-electrical efficiency of the power cycle. The thermal efficiency of gasification systems using low-temperature  $\text{H}_2\text{S}$  cleanup systems is in the range of 60 to 70%, which is less than or equal to a modern coal-fired boiler with  $\text{SO}_2$  removal. However, Robson (25) estimates that this can be raised to 85% by using high-temperature  $\text{H}_2\text{S}$  cleanup processes, which yield a 42.5% system efficiency with a high-temperature turbine. This points very clearly to the need for consideration of the combustion and emission problems associated with a high-temperature fuel gas which may also contain  $\text{NH}_3$ .

In view of the complex matrix of turbines and boilers fired with low- and high-temperature fuel gases with and without  $\text{NH}_3$ , Martin (23) chose to discuss boiler control techniques in general and gas turbines in greater detail. For the gas turbine, the case to be considered was chosen based on the most severe possible case of high turbine inlet temperature (1540°C), high fuel temperature (815°C), and high air preheat (537°C) at 10 atmospheres. The fuel was assumed to be a wet Lurgi low B.t.u. gas (see Table 2 for composition) which could have as much as 4,000 p.p.m.  $\text{NH}_3$  remaining after a hot  $\text{H}_2\text{S}$  cleanup process (25). The concept evaluation was performed using the Modular Kinetics Application Program (MKAP) developed by Ultrasystems, Inc., based on the numerical analysis method of Tyson and Kliegel (26). The MKAP program utilized a set of reaction rates which had been

compared to experimental data and was run in a mode chosen to simulate an advanced combustor concept—catalytic combustion. The key factors were as follows: (1) in a catalyst monolith each cell may be viewed simplistically as a stream tube; (2) if a significant amount of the reaction occurs in the gas phase, the thermal  $\text{NO}_x$  formation chemistry may be reasonably described by homogeneous kinetics; and (3) for a minimum heat loss from the catalyst, at steady state a nearly uniform temperature may exist over the flow path. It is also assumed that the catalyst surface does not play a significant role in the formation or destruction of either fuel or thermal  $\text{NO}$ . In addition, for this initial evaluation, the calculations were not constrained by one limit imposed by current catalysts, that is, temperature of operation. As the concepts are further developed, this limit must be faced and/or other approaches tried. The results of the calculations can be summarized as follows:

(1) For a single-stage fuel-lean case without  $\text{NH}_3$ , thermal  $\text{NO}_x$  production is very low (i.e., below 40 p.p.m.) for residence times up to 100 milliseconds, which is a very favorable result considering the severity of the conditions (see Figure 3).

(2) For the same case with 4,000 p.p.m.  $\text{NH}_3$  in the fuel about 86% was converted to  $\text{NO}_x$  (i.e., 890 p.p.m. @  $\phi = 0.45$ ), which is consistent with experimental data on other systems.

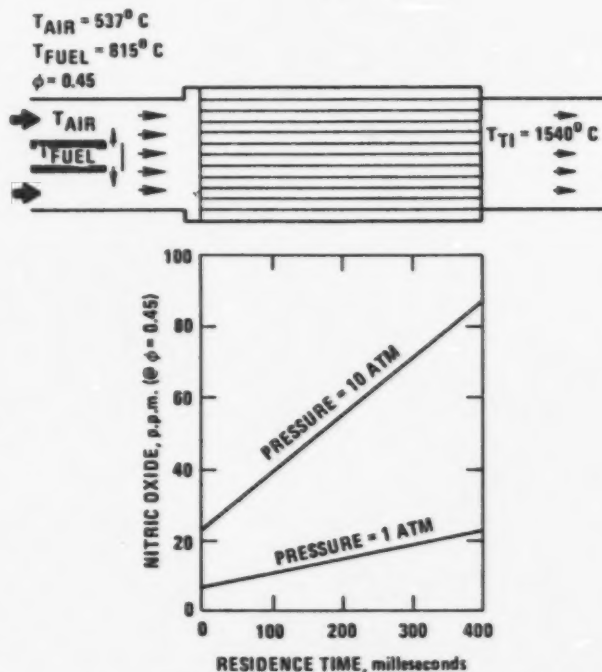


FIG. 3. FORMATION OF THERMAL  $\text{NO}$  AS A FUNCTION OF PLUG FLOW RESIDENCE TIME.

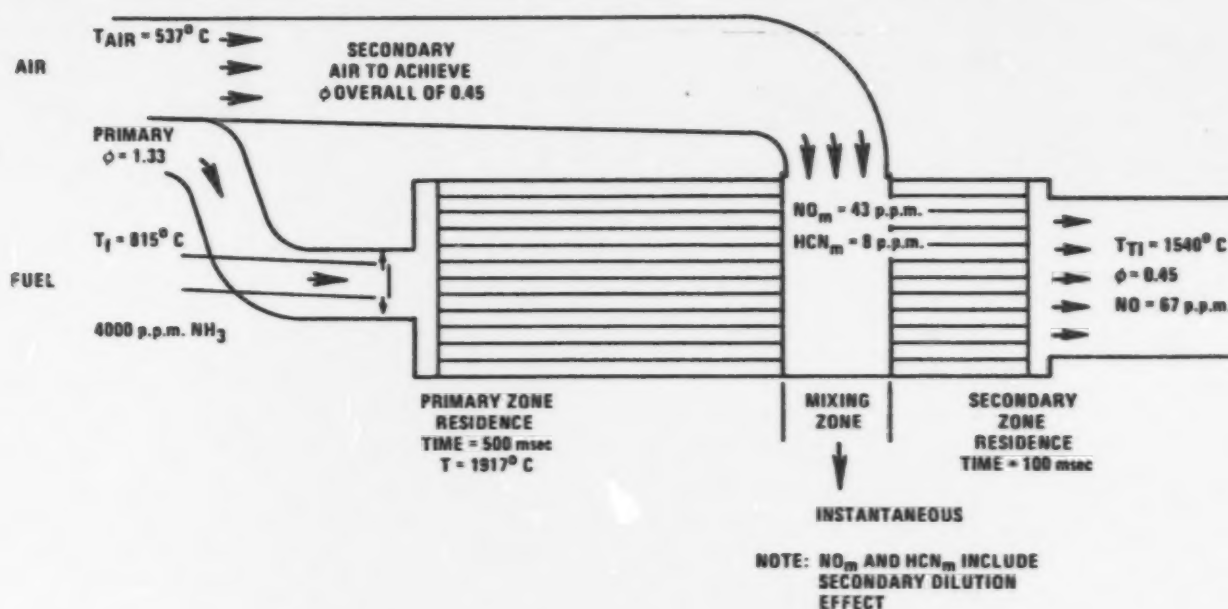


FIG. 4. OPTIMIZATION OF THE INITIAL DESIGN CONCEPT.

(3) For the 4,000 p.p.m.  $\text{NH}_3$  in the fuel, a number of staged combustion calculations were performed and an optimum design concept was identified as shown in Figure 4. Although this concept shows dramatic promise for low  $\text{NO}_x$  emissions (i.e., 67 p.p.m. @  $\phi = 0.45$ ) based on the calculations, the concept has yet to be transferred into hardware for experimental evaluation. Among the problems that may arise are the difficulties in securing a high-temperature catalyst or an alternative; in achieving long residence time in the primary zone; and in approaching the instantaneous mixing of secondary air necessary to prevent thermal  $\text{NO}$  excursions.

(4) Similar concepts should be applicable to steam generators with equal or greater success. The most closely related steam generator would be the high-pressure (supercharged) boiler; however, with the exception of size, the general approaches should be applicable to all boilers. The boiler application may be somewhat easier to accomplish as significant quantities of heat can be removed from the primary zone. This is particularly essential when the boiler must operate at low overall excess air for optimum efficiency. Otherwise, even with instantaneous secondary air mixing, the second stage temperature would be high and significant thermal  $\text{NO}$  formation could occur.

While none of the concepts discussed above are definitive, it can be seen that the design of combustors has the potential for substantial emission control, if that aspect is a consideration in laying out the concept initially. Further work is underway at the EPA (both

in-house and on contract) to explore these concepts on a combined experimental-analytical basis. This effort should clearly establish the emission reductions achievable and define many of the important factors in application of combustion techniques to alternate fuels.

#### Fluidized-Bed Combustion of Coal

Experimental studies carried out with fluidized-bed coal combustion in Britain (27) and in the United States (28) during the 1960's showed that this combustion system has the potential of meeting existing emission standards for a coal-fired, steam-raising plant. The significant improvement in these experiments compared with earlier studies was the success in controlling the bed temperature between the low temperature stability limit ( $\sim 700^{\circ}\text{C}$ ) and the higher limit set by the sintering of the coal ash ( $\sim 900^{\circ}\text{C}$ ), by means of heat exchangers immersed in the fluidized bed. The background information on pollutant formation and fuel combustion is summarized. This is followed by a detailed discussion of recent information on  $\text{NO}_x$  formation and control mechanisms. Finally, some systems applications of the technology are considered.

#### $\text{NO}_x$ Emissions

At relatively low temperatures very low  $\text{NO}_x$  emissions were expected. However, values as high as 800 p.p.m. have been reported, which are far above the equilibrium values for these temperatures and are also of the same order of magnitude as those observed for

conventional furnaces operating at much higher flame temperatures (Table 5). The reason for this lies in the mechanism by which NO is formed. In a combustion system NO may be formed by the oxidation of atmospheric nitrogen (thermal NO) and/or by the oxidation of nitrogen compounds chemically bound in the fuel (fuel NO).

TABLE 5.

CALCULATED EQUILIBRIUM CONCENTRATIONS OF NO AND NO<sub>2</sub> IN FLUE GAS ARISING FROM COMBUSTION IN AIR CONTAINING 2% v/v OF WATER VAPOR (ON THE DRY, MINERAL-MATTER-FREE BASIS THE COMPOSITION BY WEIGHT OF THE COAL TO WHICH THE CALCULATIONS RELATE IS: C 82.0%; H 5.1%; O 8.9%; N 2.0%; S 0.8%; Cl 0.2%.)

| Temperature<br>flue gas (°C) | 827  | 1427  | 1721 | 2327   |
|------------------------------|------|-------|------|--------|
| NO (p.p.m.)                  | 28.8 | 936.9 | 2427 | 10,500 |
| NO <sub>2</sub> (p.p.m.)     | 0.25 | 0.87  | 1.21 | 2.98   |

Combustion is assumed to be with 10% excess air, at 1 atm. (30)

In the case of fluidized-bed coal combustion there is experimental evidence (29, 30) supporting the second mechanism. Using a gas flame doped with nitrogenous additives and operating at temperatures similar to those in fluidized beds, Shaw (30) confirmed the contribution of the additives to NO emission. In addition, experiments at ANL showed little difference in NO whether air or argon-oxygen was used as the oxidizer, which strongly suggested that fuel NO was the primary concern (29).

There is little information available on the types of nitrogen compounds in coal. Birkof and Onywal (31) found, by chemical analysis, the following main groups: (a) 35% as urea units, amino acids, and peptides, (b) 23% as long chain amines, (c) 10% as carbazole structures (which decompose to give ammonia), and (d) 26% as nitrogen compounds which give elemental nitrogen. Kirner (32) reported that nitrogen compounds in coal are released during thermal degradation processes in two distinct stages. In the early devolatilization they consist mostly of the tar bases (pyridines, quinolines, and other heterocyclic compounds), ammonia, and free nitrogen, which can account for nearly 50% of the total nitrogen initially present in the coal. The relative amounts of these products depend on the temperature, rate of heating, rank of coal and time-temperature history of the vapors. The remaining 50% of the nitrogen is not easily removed from the coal matrix to which it seems to be linked by much stronger bonds (possibly of the type nitrile), thus staying in the char. It was also reported that experimental evidence was available showing that none of the nitrogen is in any form attached to the ash.

Kunle (33) carbonized bituminous coal at various temperatures and measured the amount of nitrogen remaining in the coke at each temperature (Table 6).

TABLE 6.  
EFFECT OF CARBONIZING TEMPERATURE ON THE  
AMOUNT OF NITROGEN REMAINING IN THE CHAR. (33)

| Temp. (°C)   | N remaining<br>in the coke<br>(dry, ash-free) % |
|--------------|-------------------------------------------------|
| 500 to 520   | 1.49                                            |
| 520 to 530   | 1.17                                            |
| 550 to 560   | 1.49                                            |
| 600 to 620   | 1.31                                            |
| 650 to 670   | 1.26                                            |
| 690 to 710   | 1.39                                            |
| 750 to 770   | 1.19                                            |
| 800 to 820   | 1.02                                            |
| 850 to 875   | 1.41                                            |
| 900 to 930   | 0.72                                            |
| 950 to 975   | 0.94                                            |
| 1000 to 1020 | 0.47                                            |

% N in original coal: 1.71 (dry, ash-free)

Juntgen and Klein (34) describe pyrolysis tests in which they found that 20% to 50% of the total nitrogen is separated, in elemental form, when the coal is heated to 1000°C, depending on the coal rank (anthracite to high volatile). They attributed this nitrogen to the decomposition of aliphatic nitrogen compounds. The remaining 80% to 50% could be released only by fracturing the C-N bonds by the attack of oxygen, and it was postulated that this remaining nitrogen has a heterocyclic nature.

From these studies we can expect that the mechanism by which N-compounds in coal are oxidized can change greatly during the entire burning time of a coal particle.

### Combustion Efficiency

Conditions for the burnout of char in fluidized beds are favorable because of the good solids recirculation and long residence time. The largest loss of carbon from the bed is caused by the elutriation of combustible particles. Larger particles which are carried away by the fluidizing gas can be precipitated from the gas and recycled into the bed, while small particles can be introduced into so-called carbon burnup cells with lower fluidizing velocities as recommended by Bishop (35) and reported by Robinson et al. (28). The amount of carbon burning in the freeboard above the bed is small, less than 7%, due to the relatively short residence time, low temperature, and low oxygen concentration.

At low bed temperature the reaction rate for oxidation of CO is slow and the gas residence time is too short to allow complete burnout. Incomplete mixing of combustibles and air may be another factor in unburned CO's escaping from the bed. The combustion of CO will go to completion as the bed temperature is raised to about 800°C and the excess air level reaches 20%. Because of the relatively poor lateral mixing in the freeboard a small amount of air (e.g., 10% of fluidizing gas) or recirculated combustion products used for the stirring of the freeboard by jets can be effective in reducing CO emission. The fraction of very fine coal particles in the feed coal has an important effect on the combustion efficiency. Fine particles in the feed coal has an important effect on the combustion efficiency. Fine particles will increase the carry over losses and also the CO emission from the bed. Gibbs and Beer (36) reported detailed experimental data on the effects of operating variables such as fluidizing velocity, bed temperature, coal type, and excess air upon the combustible losses obtained in a 30 x 30-cm fluidized combustor. The main conclusions can be summarized as follows:

(1) The combustible losses decrease with fluidizing velocity, bed temperature, and excess air but are independent of freeboard temperature. For a bed temperature of 800°C and an excess air level of 25% the major combustible losses (6% of feed combustibles) are due almost entirely to elutriation, and even large increases in excess air beyond 25% produce only a slight reduction in the combustible losses. In order to reduce the elutriation loss to an acceptable level (2%) the elutriated particles should either be returned to the bed or burned in a separate combustor.

(2) The CO concentration in the flue gases is dependent on the volatile content of the coal feed and its size distribution; lower CO concentrations are associated with a low volatile feed and the absence of fines in the feed.

(3) The elutriation loss is increased if low volatile char or coarse coal is used as feed to the bed, probably due to an increase in the particulate combustibles in the bed.

(4) The total elutriation loss is also attributed to the splashing of particles larger than the critical elutriation size from the combustor. In order to suppress the latter loss it may be beneficial to insert baffles in the freeboard or to increase the height of the freeboard.

(5) A large proportion of the coal (50%) appears to be consumed in the first 150 mm of the bed close to the coal feed point followed by a gradually decreasing rate of combustion as the bed surface is approached.

(6) Further combustion, mainly CO oxidation, takes place in the freeboard and this increases the

temperature immediately above the bed by 25°C. The proportion of combustion in the freeboard decreases with excess air and is small in comparison to that in the bed, being no more than 7% of the total combustion.

### Formation and Control of NO<sub>x</sub>

Following earlier experiments on NO emissions from fluidized coal combustion carried out at Argonne (29), at Esso (37), and at Pope, Evans and Robbins (28), more detailed studies started at Sheffield in 1972. The objectives of the research were to obtain information on the mechanisms of formation and destruction of NO based on measurements of spatially- and time-resolved species concentration and temperature in a pilot-plant-sized (30x30-cm) and a bench-type (7.5-cm-dia.) fluidized bed (5, 36, 38, 39, 40).

Experiments were carried out with a wide range of coal types: anthracites, bituminous coals, and chars. The bituminous coal was similar to that used in the ANL studies, which was a high volatile bituminous Pittsburgh seam coal from the Consolidation Coal Company's Arkwright mine. The coal used in the Sheffield experiments was also a bituminous coal but with the particle sizes between 1,000 and 3,000  $\mu\text{m}$ . The analysis (as received) was 19.8% ash, 33.4% volatiles, and 6.8% moisture by wt. The nitrogen content was 1.5% (dry basis), and the sulfur was 1.7% (dry basis). The important findings of the Sheffield studies are summarized below.

**Measurements of NO Concentration Distribution.** Figure 5 shows that there is rapid production of NO immediately above the distributor plate. Because of the plug-flow-type gas concentration distribution, the O<sub>2</sub> concentration is always high at the bottom of the bed so that NO formation rates are high there irrespective of the input fuel/air ratio. Higher up, in the froth layer of the bed and in the freeboard, the NO concentration of the gas is reduced. This reduction, however, is dependent upon the overall fuel/air ratio (Figure 5). The NO concentration profiles show also a significant radial NO concentration gradient. This is consistent with the physical model, in that the NO formation takes place mainly in the particulate phase and in that the probability of sampling bubble phase gas is higher in the center than near the walls of the fluidized bed.

**Source of NO.** The respective contributions of the volatile matter and the char to the NO formed and the homogeneous and heterogeneous NO reduction mechanisms were studied in a 7.5-cm batch fluidized

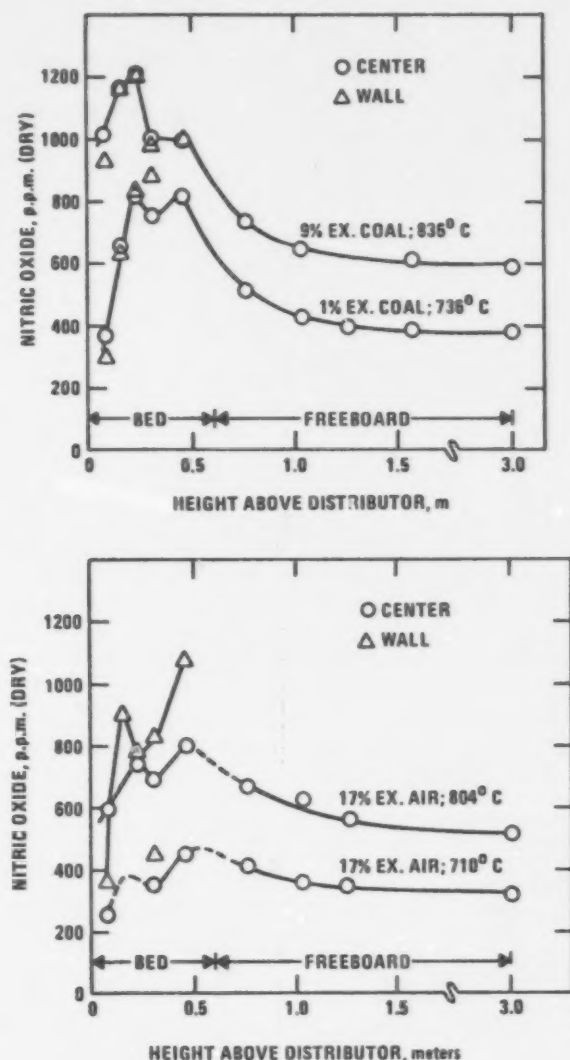


FIG. 5. AXIAL NO CONCENTRATION PROFILES AT THE WALL AND CENTER OF THE 30-cm x 30-cm COMBUSTOR (36).

bed (5). Figure 6 shows a typical pulse of NO when a batch of coal particles is burned in the bed. From comparison with Figure 7 it can be seen that the total NO emission is composed of an initial sharp peak due to combustion of volatiles evolved at that bed temperature followed by a shoulder characteristic of a much slower process, the char burning. It will be shown later that the amount of volatiles is dependent on the bed temperature. The visible burnout time (measured with a stopwatch) coincided to within  $\pm 5\%$  of the pulse time.

It is seen in Figure 7 that when the coal is first pyrolyzed in argon a small peak of NO is detected: as there was no oxygen in the carrier gas (confirmed by chemical analysis) this peak was due either to oxygen absorbed on coal or to easily decomposable and partially oxidized N-compounds formed during storage of

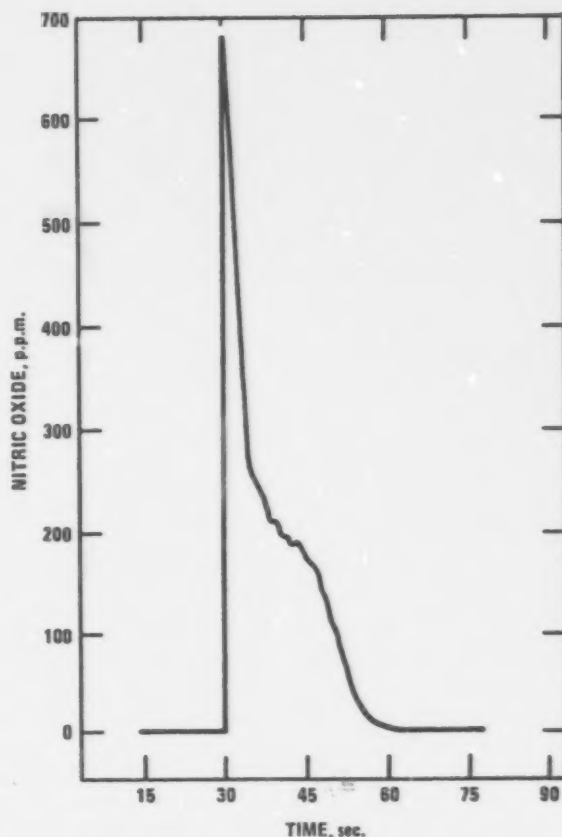


FIG. 6. NITRIC OXIDE PULSE DURING THE COMBUSTION OF A BATCH OF COAL PARTICLES IN THE 7.5-cm-DIA. FLUIDIZED BED (38).

coal in air. This is in agreement with previous measurements of NO in coal carbonization (41). These easily decomposable compounds react with NO itself, so high rates of heating reduce the contact of the released NO with those compounds yielding higher NO concentrations; it was observed that the small initial peak increased with temperature (38). Once volatile species have parted with their parent coal particle the chances of their further reaction by chemisorption on other coal particles in the bed are reduced and are therefore little dependent upon the residence time of the gas in the bed or on the fluidizing velocity. The same technique made it possible to compare the total NO emission index when burning in air and when burning in a mixture of argon and oxygen. Figure 8 shows the ratio of the two as a function of bed temperature. In Figure 9 the NO emission index is plotted for coal and char burning, respectively, as a function of bed temperature. The char is generated by devolatilizing the coal in the bed at the specified temperature under inert conditions. The char NO is then determined by switching to oxidizing conditions. The total NO is

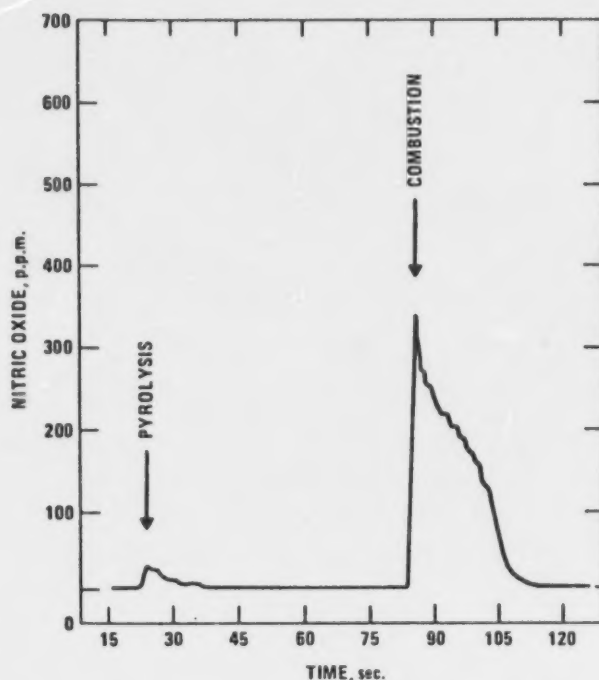


FIG. 7. NITRIC OXIDE PULSES DURING (1) PYROLYSIS IN ARGON, (2) BURNING IN A MIXTURE OF ARGON AND OXYGEN, OF A BATCH OF COAL PARTICLES IN THE 7.5-cm-DIA. BED (38).

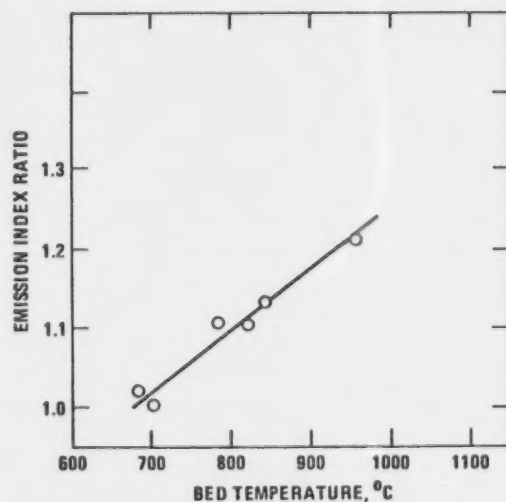


FIG. 8. RATIO OF TOTAL EMISSION INDEXES (VOLATILES AND CHAR) OBTAINED WHEN A BATCH OF COAL PARTICLES IS BURNED IN AIR AND WHEN BURNED IN A MIXTURE OF 21% + 79% ARGON, AS A FUNCTION OF TEMPERATURE (38).

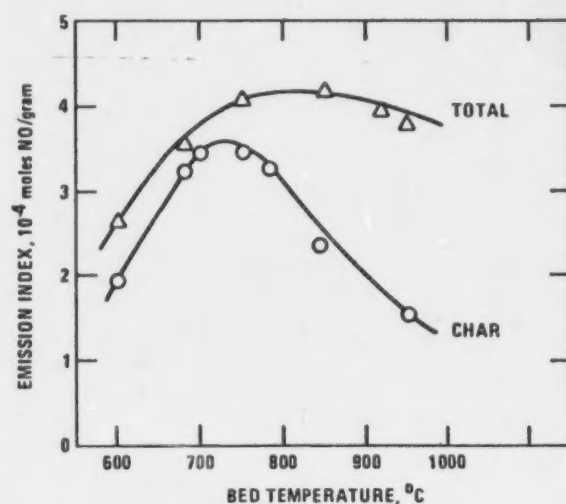


FIG. 9. TOTAL AND CHAR EMISSION INDEXES AS A FUNCTION OF BED TEMPERATURE (38).

determined by introducing the coal to the bed initially under oxidizing conditions. The difference in the NO emissions is related to the amount of nitrogen driven off in the volatiles when the char is generated and increases as the devolatilization temperature goes above 750°C. This is as expected: the volatile yield from a given coal increases when the final temperature of the pyrolysis is higher (42). Further evidence of this is shown in Figure 10. Here the emission index is given as a function of temperature for char generated in two different ways. One char came from coal pyrolyzed in argon and burned at the same bed temperature by the addition of

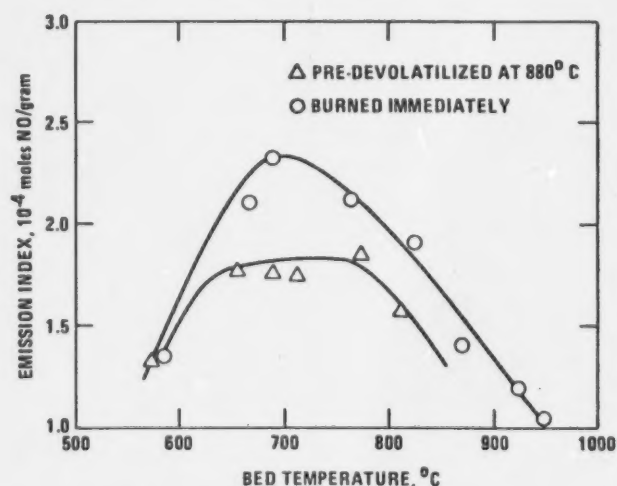


FIG. 10. EFFECT OF TEMPERATURE ON CHAR NO EMISSION (5).

oxygen to the fluidizing gas; the other, from coal devolatilized at a temperature of 880°C and burned at varying bed temperatures. The NO emission is significantly less when the char has been devolatilized at a temperature higher than its combustion temperature, which demonstrates the relationship of temperature to the amount of nitrogen evolved in the volatiles.

The reduction of NO concentration due to homogeneous (i.e., NO plus volatile) and heterogeneous (i.e., NO plus solid matter) reactions was investigated in the batch-type fluidized bed (43). In Figure 11, curve 1 represents the NO pulse of a burning

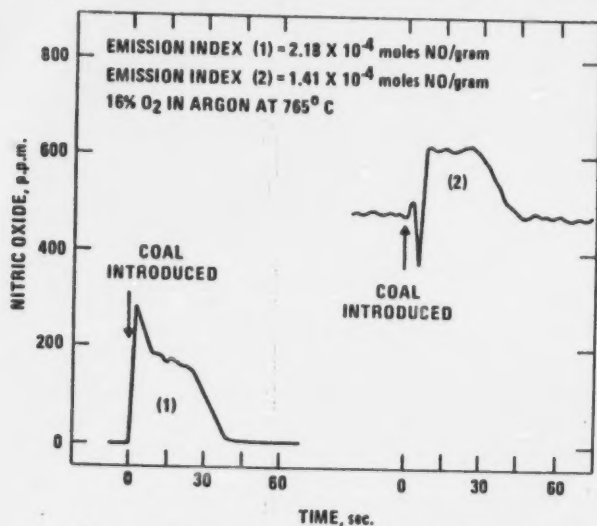
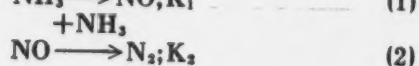
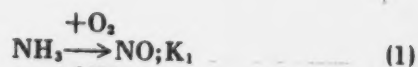


FIG. 11. EFFECT OF 470 p.p.m. INLET NO ON NO PULSES (5).

batch of coal particles. When 470 p.p.m. NO was introduced into the fluidizing gas (16% O<sub>2</sub> in argon) at 765°C, the initial peak due to volatiles is reversed, showing that the volatile matter is reducing the NO in the fluidizing gas (curve 2). It is calculated that the result of the volatile-NO reaction was to reduce the conversion of fuel nitrogen from 21.8% to 14.1%, even under overall oxidizing conditions. The homogeneous reaction most likely to be responsible for the NO reduction is that between nitrogenous fragments and NO. In the case of amines a kinetic mechanism has been proposed and the rate constants were determined by DeSoete (44). The reaction mechanism involves two parallel-consecutive reactions in which NO is formed by oxidation of fuel-N fragments and is subsequently destroyed by these same fragments:



where

$$K_1 = 3.1 \times 10^7 \exp\{-30000/RT\} \text{ and}$$

$$K_2 = 8 \times 10^7 T^{-1/3} \exp\{-27000/RT\}$$

The details of the mechanism are shown by the scheme in Figure 12. A similar mechanism was proposed for cyanogen compounds (44).

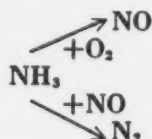


where

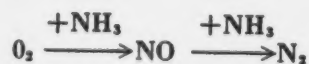
$$K_1 = 9 \times 10^{-14}, \text{ and}$$

$$K_2 = 8 \times 10^{-13} \text{ cm}^3/\text{moles/sec at } \sim 1727^\circ\text{C.}$$

In this mechanism the fuel-N takes part in two parallel reactions, i.e.



whereas NO is an intermediate in two consecutive reactions, i.e.



It can therefore be expected that the mixing pattern in the reactor will affect the products' (NO, N<sub>2</sub>) distribution. The formation of the intermediate product (NO) can be minimized by backmixing or recirculation of the NO into the devolatilization zone for reduction. Analytical calculations were carried out which confirm this effect of backmixing (43).

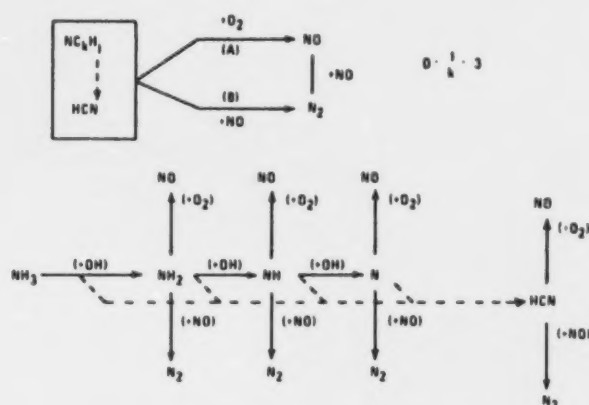


FIG. 12. DUAL-STEP MECHANISM OF FUEL-NITROGEN OXIDATION (5).

The interaction between char and NO was studied both in the presence and absence of  $\text{O}_2$  in the fluidizing gas. In Figure 13 curves 1 and 2 were obtained in experiments similar to those carried out with coal by using devolatilized char. The results show a strong reduction of NO by the char under  $\text{O}_2$ -deficient conditions and some reduction in the initial time period after  $\text{O}_2$  is injected. The strong temperature dependence of the NO-char reaction is shown in Figure 14, where the conversion of NO to  $\text{N}_2$  has been plotted as a function of fluidized-bed temperature. (These latter data were obtained in the absence of  $\text{O}_2$  in the gas.) Figure 15 represents the fraction of NO decomposed as a function of time. Immediately after a batch of char particles was

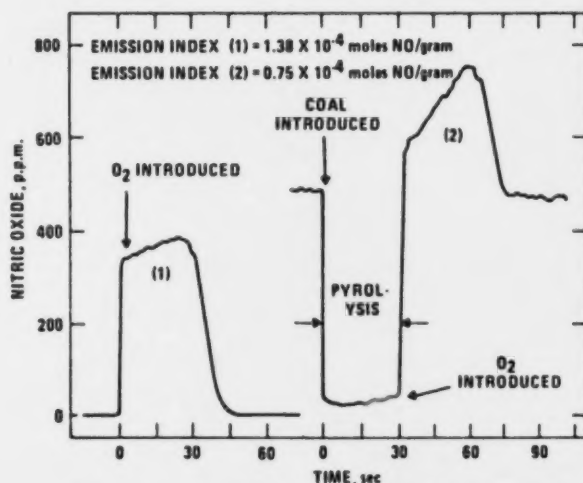


FIG. 13. EFFECT OF 470 p.p.m. INLET NO ON NO PULSES (5).

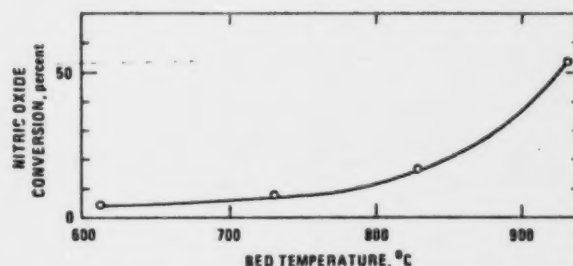


FIG. 14. REDUCTION OF 770 p.p.m. NO IN ARGON BY CHAR (7).

dropped in the bed the NO concentration of the effluent gas was reduced by about 70%. As a function of time, however, the effectiveness of the char is gradually diminishing. Gasification experiments of char with NO have shown CO and  $\text{CO}_2$  formation at fluidized-bed operating temperatures (43) so that this reaction may well be responsible for the NO reduction. The high initial rate and the apparent saturation of the char with

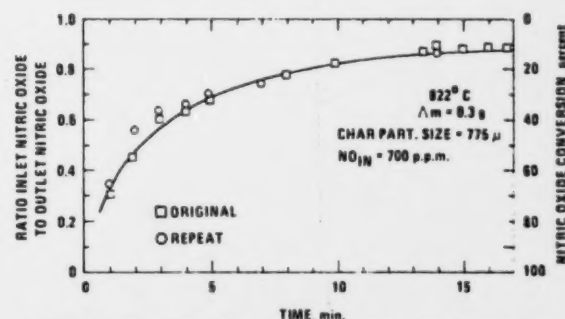


FIG. 15. RATIO BETWEEN THE OUTLET AND THE INLET NO CONCENTRATIONS AND PERCENT CONVERSION, AS A FUNCTION OF THE LENGTH OF THE RUN (40).

time can not, however, be explained from these studies. The significant influence of the char particle size upon the percent reduction of NO in the absence of  $\text{O}_2$  is illustrated by Figure 16. With large particles ( $>100\mu$ ) the reaction can be expected to be controlled by boundary-layer-type diffusion. For smaller particles activated absorption might become the rate-determining step with the consequence that the specific rate of reaction becomes independent of particle size. In addition the readily available surface area of the coal is significantly increased as the particle size is decreased. This is consistent with models of microheterogeneous reactions of coal at these temperatures (45). The effect of the fluidizing gas velocity upon NO emission is

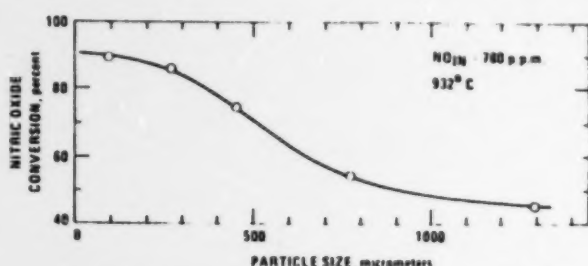


FIG. 16. THE EFFECT OF CHAR PARTICLE SIZE ON THE CONVERSION OF NO (40).

twofold: (1) the initial rise of the curves in Figure 17 can be attributed to an increasing supply of oxygen and also to the shortened residence time, which affects adversely the reduction of the NO by the char; and (2) the drop in NO emission observed at higher velocities is due to increased backmixing with rising fluidizing velocity and is consistent also with a physical model of

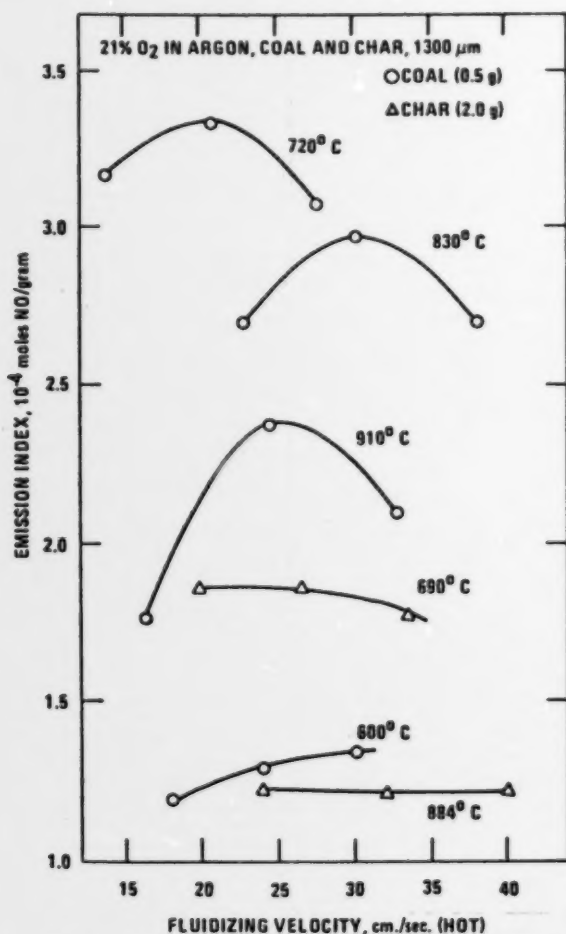


FIG. 17. EFFECT OF FLUIDIZING VELOCITY ON NO EMISSIONS (5).

the NO formation and destruction reactions of coal volatiles and char (5), Figure 18. According to this model, part of the NO is formed during the oxidation of volatile nitrogen outside the particle boundary layer. It follows from the nature of the kinetic mechanism shown in the upper half of Figure 18 that increased mixing of the gas in the bed results in reduced NO emission. The maximum NO emission can be expected

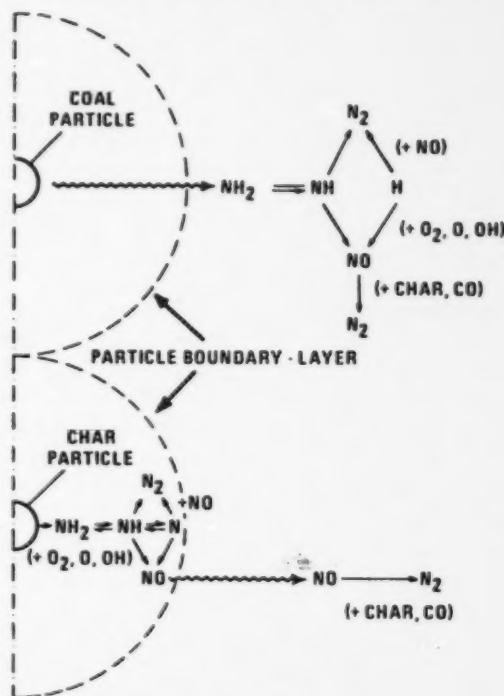


FIG. 18. PHYSICAL MODEL DESCRIBING A MECHANISM OF NO GENERATION DURING THE BURNING OF A COAL PARTICLE (5).

when the gas is considered to be in plug flow. This is because NO is an intermediate product of a two-step parallel-consecutive series of reactions. In such a reaction system the yield in the intermediate product is known to decrease with increased mixing state of the gas (46). In contrast to the NO reaction of volatile matter and NO, the reaction between char and NO will take place mainly within the stagnant boundary layer surrounding the particle. The reaction will not be dependent on gas mixing since conditions within the boundary layer are little affected by changes in gas velocity and mixing in the main stream; however, it is significantly influenced by temperature and fuel particle size.

Staged combustion (i.e., secondary air injection into the freeboard) is also an effective method of reducing NO emission from coal-fired fluidized beds. Figure 19 shows results of experiments carried out with a rich overall stoichiometry in the bed and secondary air injected through an array of nozzles into the freeboard

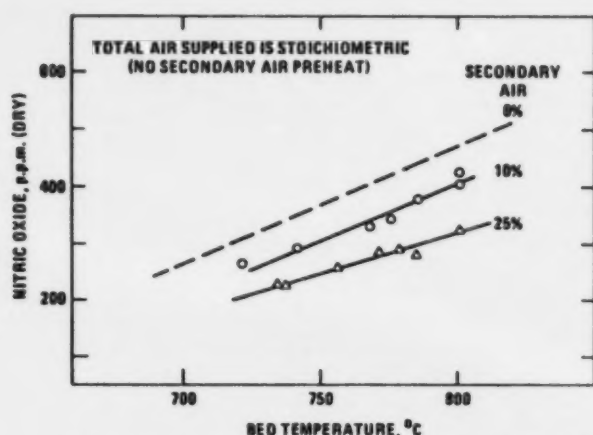


FIG. 19. THE EFFECT OF SECONDARY AIR INJECTION INTO THE FREEBOARD ON NO EMISSION (40).

(40) for two levels of staging. It illustrates the significant reductions in NO emission due to the rich primary reaction zone. Also with staged combustion the better mixing in the freeboard gives improved burnout of CO, which in turn enables the overall excess air to be reduced.

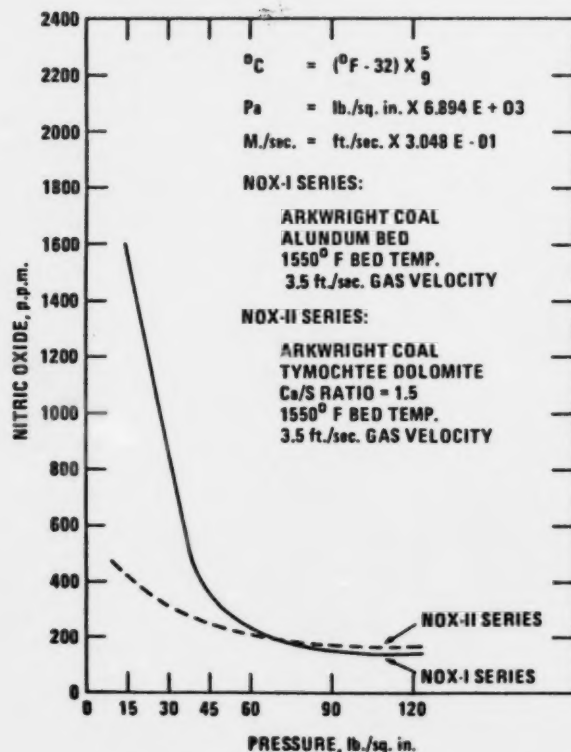


FIG. 20. EFFECT OF PRESSURE ON NO WITH INERT AND DOLOMITIC BED MATERIALS (49).

Results of experiments at Exxon (47), BCURA (48), and ANL (49) are in agreement that significant reductions in NO emission are observed under elevated bed pressure. Figure 20 shows the effect of total pressure upon the NO concentration of the flue gas as determined by Vogel et al. in ANL's bench-scale, pressurized fluidized combustor. The lower NO emission is attributed to more effective NO reduction processes since the bubbles are smaller in pressurized beds because of unfavorable hydrodynamic conditions for stability of larger bubbles. This in turn results in improved interphase mass transfer. In addition, pressurized beds are usually taller, which improves further conditions for gas/solid contact.

**Sulfur Oxides.** The effect of both sulfur oxides and the bed material on the NO emission was investigated in several research projects (28, 29, 37). Although the results are somewhat conflicting they show a potential for reducing NO emission by the choice of suitable additives for sulfur removal. Hammons and Skopp (37) reported NO emissions as a function of run times and bed materials. They used CaO, alundum, and CaSO<sub>4</sub>. The NO emission was lowest for CaSO<sub>4</sub> as bed material. For the CaO bed, the NO emission steadily decreased with time and had reached the same level as that for the CaSO<sub>4</sub> in the bed, while the SO<sub>2</sub> concentration in the gas was increasing. They pointed to the possibility that CaSO<sub>4</sub> was a selective catalyst for the NO decomposition and that NO and SO<sub>2</sub> might be reacting to produce a reduced NO emission. The Esso researchers (37) were able to show NO reduction by SO<sub>2</sub> injection when using 20% sulfated lime as bed material. They have also demonstrated that NO can be reduced catalytically by CO in the presence of CaSO<sub>4</sub>. Research at the ANL by Jonke (29) showed that a 30% to 40% reduction of NO was possible in the presence of limestone. He also found that the reduction of NO became effective only some time after the limestone injection. It was suggested that this initial period of time was necessary for the formation of CaSO<sub>4</sub> by the reaction between the limestone and the SO<sub>2</sub> in the gas. With higher Ca/S ratios the NO reduction decreased, which is consistent with the lower concentrations of CaSO<sub>4</sub> in the bed and of SO<sub>2</sub> in the gas as the Ca/S ratio in the bed increases.

**Power Generation Cycles.** Pressurized fluidized-bed operation can be used conveniently for gas turbine or combined gas turbine/steam cycles. Many thermodynamic cycles can be so composed. Two of the most widely discussed systems are mentioned here (50, 51). In the first of these the fluidized bed is cooled by compressed air contained in heat-exchanger tubes which are immersed in the bed. In the second group steam is used as the cooling medium. The former system lends itself to gas turbine cycle applications

(Figures 21 and 22) and the latter to combined steam/gas turbine cycles (Figure 23). The gas turbine cycles can be open (i.e., the combustion products enter the gas turbine after gas clearing) or closed with air (preheated in heat exchangers) as the working medium.

Figure 23 represents a scheme of a combined steam/gas turbine cycle. Here the gas turbine cycle is

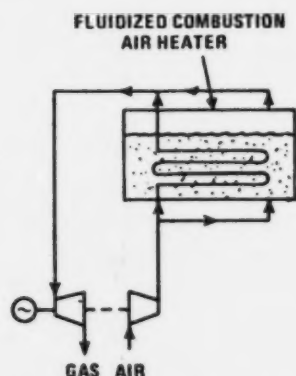


FIG. 21. OPEN AIR-HEATER CYCLE (51).

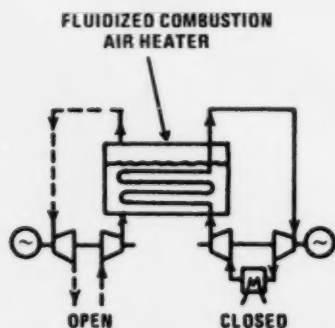


FIG. 22. SUPERCHARGED CLOSED CYCLE (51).

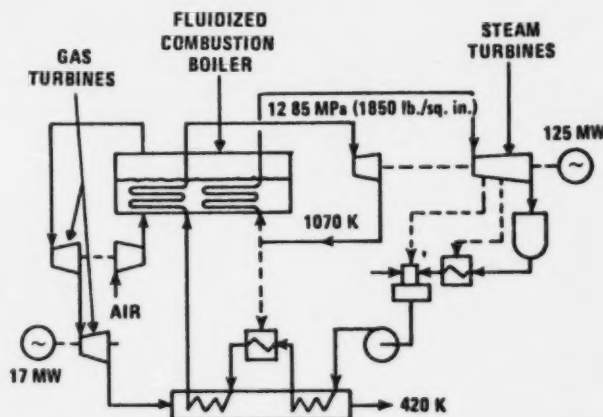
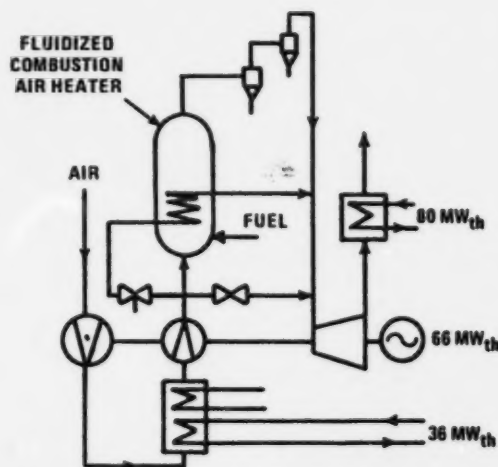


FIG. 23. SUPERCHARGED COMBINED STEAM/GAS TURBINE CYCLE (51).

FIG. 24. 66 MW<sub>e</sub> AIR-HEATER CYCLE WITH HEATING RECOVERY FOR DISTRICT HEATING (51).

open and the fluidized bed is cooled by steam, which is the working medium in the steam part of the combined cycle. Some of these cycles can be used also for energy storage and waste heat recovery. For example, in the air-heater cycle in Figure 24 the bulk of the sensible heat (remaining in the exhaust gas after the gas turbine) is recovered in a waste heat boiler. The power-generating efficiency without steam raising is 27.7%, which increases to an overall thermal efficiency of 72% by the contribution of the waste heat recovery. It has been estimated that the capital cost of this plant would be only 65% of that for the equivalent coal-fired steam plant with back-pressure turbine and stack gas clearing.

An attractive power-generating system for longer duration peak loads suitable for coal or residual oil firing involves air storage. At peak periods the compressed air is supplied from an air storage system (e.g., underground cavity) so that the whole gas turbine output is available for power generation. (Normally about two-thirds of the turbine's output is required for driving the compressor.) During off-peak periods the electric generator (acting as a motor) drives the compressor for storing the compressed air. The general advantages claimed for the pressurized fluidized combustion of coal for gas turbine and combined cycle applications are

that (1) low plant heating rates can be achieved with combined cycles incorporating fluidized combustion, which in turn reduces air pollution per unit of electricity or heat generated; (2) plant cost is reduced; (3) because of the relatively low temperature in the fluidized bed the coal ash does not sinter but remains friable, which reduces erosion in the gas turbine (also, there is little or no vaporization of alkali and silicon compounds which, on condensation in high temperature systems, form fine, submicron-sized particulates and constitute a health hazard); and (4) the particle size of the coal feed is about an order of magnitude larger than that in pulverized combustion, which eases the problem of gas/solid separation before entry to the gas turbine.

### Summary

The discussion above covers many of the aspects of emission control and application of fluidized-bed combustion of coal. It also allows the identification of areas where additional information is required for process optimization. The problems of NO emission are inseparable from those of the interphase mass transfer, of coal devolatilization and combustion kinetics, and of the reactions of sulfur oxides and sorbents in the fluidized bed. Some areas of concern are discussed below.

**Interphase Mass Transfer.** The interaction between the gas phase and solids in the bed has unresolved areas, including the following questions, (1) How do bubble size, frequency of bubble shedding, bubble growth, and coalescence depend upon distributor type, fluidizing velocity, bed and immersed-tube geometry, and total pressure? (2) What is the role of bubbles in oxygen bypassing? (3) What is the role of bubbles in particle mixing? (4) What is the relative magnitude of particle mixing time and char burnout time? (5) What is the importance of these factors in determining the spacing of coal feed points?

**Kinetics of Combustion.** A number of details of fuel devolatilization and subsequent reaction need to be addressed, including the following questions, (1) What are the processes that govern the escape of the volatile matter? (2) If particle mixing time is commensurable with volatile evolution time, does the volatile matter burn in the vicinity of the particle or does it react with the bubble oxygen and burn as a diffusion flame at the bubbly boundary? (3) What are the processes that control particle elutriation from the bed? (4) What proportion of the volatiles and particles burn in the freeboard?

**NO<sub>x</sub> Emissions.** Additional knowledge is required to achieve the maximum reduction of NO<sub>x</sub>. Specific questions include: (1) What are the detailed mechanisms of fuel-N evolution and oxidation in the fluidized bed? (2) What are the detailed mechanisms of

the homogeneous reactions leading to the destruction of NO in fluidized beds? (3) How does the SO<sub>2</sub> concentration in the bed affect the fuel nitrogen oxidation and destruction reactions? (3) What is the effect of the type of sorbent? (4) What is the detailed mechanism of the NO/char reaction? (5) How should the fluid dynamics of the bed be varied for further reduction of NO emission without adversely affecting combustion efficiency? (6) What are the details of the NO formation and destruction processes at elevated pressure? (7) If the improved interphase transfer is responsible for the reduced NO emission under conditions of elevated pressure, how can this information be used for improved design and operation of atmospheric fluidized combustors?

These and many other questions concerning the engineering development of fluidized combustors will have to be answered if the full potential of fluidized-coal combustion is to be realized in industrial applications in the 1980's.

### CONCLUSIONS

Based on the discussion presented in this paper, the following conclusions are drawn:

#### Alternate Fuels

This is an emerging technology and the available information on combustion and emission characteristics is limited. The following points are based on the existing information.

(1) High-B.t.u. gaseous fuels are likely to be similar to conventional fossil fuels, and current combustion technology should be directly applicable. This conclusion may be modified somewhat by the potential for the presence of H<sub>2</sub> in SNG; however, it may be beneficial, particularly from the standpoint of burner stability.

(2) Low-B.t.u. gaseous fuels from which nitrogen compounds (e.g., NH<sub>3</sub>) are removed are likely to have low NO<sub>x</sub> emissions. The main areas of concern will be burner design for stability and furnace design to achieve required heat transfer. If for any reason staged combustion or any other technique that results in fuel-rich zones is used, there may be NO<sub>x</sub> generation by formation and subsequent oxidation of nitrogen compounds for fuels containing significant methane.

(3) Only a limited amount of information is available on combustion of LBG containing nitrogen compounds; however, experience with other fuels indicates that a substantial conversion of the NH<sub>3</sub> to NO<sub>x</sub> can be expected if proper design approaches are not used. No data on specific attempts to control fuel NO<sub>x</sub> in low-B.t.u. gas combustion is currently available; therefore, the results of an attempt to use an existing computational approach for evaluation of design concepts to control NO<sub>x</sub> are summarized. The

staged combustion approach shows good potential; however, the concept requires experimental validation and consideration of many practical aspects.

(4) Perhaps the most important point is that the combustor design concepts represent a significant departure from current gas turbine combustors; however, it may be necessary to abandon conventional design approaches to achieve control of  $\text{NO}_x$  emissions for the severe conditions imposed by the advanced power generation systems.

(5) While control technology has not been assessed for  $\text{NO}_x$  emissions for high-nitrogen synthetic liquid fuels, it appears that similar concepts should apply. The major uncertainties are in the area of fuel properties related to smoke formation and/or particulate resulting from the carbon-to-hydrogen ratio of the fuel and from the solid material remaining in the fuel following refining. If combustion control of fuel  $\text{NO}_x$  can be used, it will reduce the necessity for hydrotreating the synthetic fuels to remove nitrogen compounds.

#### Fluidized-Bed Combustion

The conclusions of experimental and recent theoretical research can be given as follows:

(1) The emissions of  $\text{NO}_x$  from fluidized-bed combustion have the potential of meeting the existing standards for coal-fired steam-generating plant (i.e., 1.26 gm of  $\text{NO}_x$  as  $\text{NO}_2/10^6$  Cal).

(2) Under the operating conditions of the fluidized-bed combustor, up to 90% of the  $\text{NO}_x$  formed is fuel NO.

(3) NO is generated both during the volatile and the char combustion. The nitrogen left in the residual char decreases as the devolatilization temperature rises.

(4) NO is formed preferentially near the coal inlet point where the oxygen concentration is high irrespective of the input stoichiometry. NO emission is therefore a weak function of input stoichiometry. In the temperature range between 660 and 850°C the NO emission increases linearly with temperature at an approximate rate of 2.3 p.p.m./°C.

(5) NO is reduced by reaction with nitrogenous fragments in the volatiles and also by the heterogeneous reaction with char. The latter reaction is strongly temperature dependent and becomes significant only above 800°C.

(6) Staged combustion has beneficial effect on  $\text{NO}_x$  emission: 10% secondary air injection resulted in a 20% reduction in  $\text{NO}_x$  emission.

(7) NO emission from pressurized fluidized combustion is much lower than from atmospheric pressure beds. This is most likely due to the improved interphase mass transfer and thus more effective NO reduction under conditions of elevated pressure.

(8) The technology is still in the experimental stage and practical application remains to be accomplished.

#### General

The two technologies discussed offer different paths to utilization of the U. S. coal resources in an environmentally acceptable manner. The following points should be emphasized.

(1) Current utilization of coal is by direct pulverized or stoker firing with stack gas cleaning for  $\text{SO}_2$  control. Physical and chemical coal cleaning is also being developed for coal desulfurization prior to combustion. The control of  $\text{NO}_x$  is accomplished by combustion modification, and advanced technology for the higher levels of control is being developed. The manufacturing and operational experience for these conventional approaches is well established, and the two alternatives discussed must compete with it.

(2) The acceptance and widespread use of the alternate approaches will depend on their ability to show a superior combination of attributes related to environmental aspects, overall process efficiency, general availability, cost, and satisfactory operability. This ultimate assessment remains to be done.

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